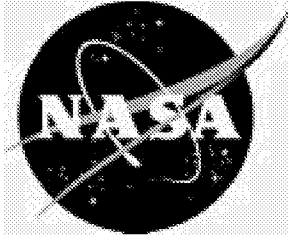


NASA/CR-2003-212147



Dynamic Mechanical Characterization of Thin Film Polymer Nanocomposites

Helen M. Herring
Lockheed Martin Engineering & Sciences, Hampton, Virginia

January 2003

The NASA STI Program Office ... in Profile

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA Scientific and Technical Information (STI) Program Office plays a key part in helping NASA maintain this important role.

The NASA STI Program Office is operated by Langley Research Center, the lead center for NASA's scientific and technical information. The NASA STI Program Office provides access to the NASA STI Database, the largest collection of aeronautical and space science STI in the world. The Program Office is also NASA's institutional mechanism for disseminating the results of its research and development activities. These results are published by NASA in the NASA STI Report Series, which includes the following report types:

- **TECHNICAL PUBLICATION.** Reports of completed research or a major significant phase of research that present the results of NASA programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers, but having less stringent limitations on manuscript length and extent of graphic presentations.
- **TECHNICAL MEMORANDUM.** Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.
- **CONTRACTOR REPORT.** Scientific and technical findings by NASA-sponsored contractors and grantees.

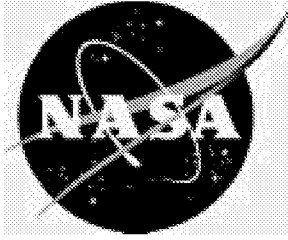
- **CONFERENCE PUBLICATION.** Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.
- **SPECIAL PUBLICATION.** Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.
- **TECHNICAL TRANSLATION.** English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services that complement the STI Program Office's diverse offerings include creating custom thesauri, building customized databases, organizing and publishing research results ... even providing videos.

For more information about the NASA STI Program Office, see the following:

- Access the NASA STI Program Home Page at <http://www.sti.nasa.gov>
- E-mail your question via the Internet to help@sti.nasa.gov
- Fax your question to the NASA STI Help Desk at (301) 621-0134
- Phone the NASA STI Help Desk at (301) 621-0390
- Write to:
NASA STI Help Desk
NASA Center for AeroSpace Information
7121 Standard Drive
Hanover, MD 21076-1320

NASA/CR-2003-212147



Dynamic Mechanical Characterization of Thin Film Polymer Nanocomposites

Helen M. Herring

Lockheed Martin Engineering & Sciences, Hampton, Virginia

National Aeronautics and
Space Administration

Langley Research Center
Hampton, Virginia 23681-2199

Prepared for Langley Research Center
under Contract NAS1-00135

January 2003

The use of trademarks or names of manufacturers in the report is for accurate reporting and does not constitute an official endorsement, either expressed or implied, of such products or manufacturers by the National Aeronautics and Space Administration.

Available from:

NASA Center for AeroSpace Information (CASI)
7121 Standard Drive
Hanover, MD 21076-1320
(301) 621-0390

National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161-2171
(703) 605-6000

Dynamic Mechanical Characterization of Thin Film Polymer Nanocomposites

Helen M. Herring
Lockheed Martin Engineering & Sciences
Hampton, Virginia

Abstract

Many new materials are being produced for aerospace applications with the objective of maximizing certain ideal properties without sacrificing others. Polymer composites in various forms and configurations are being developed in an effort to provide lighter weight construction and better thermal and electrical properties and still maintain adequate strength and stability. To this end, thin film polymer nanocomposites, synthesized for the purpose of influencing electrical conductivity using metal oxide particles as filler without incurring losses in mechanical properties, were examined to determine elastic modulus and degree of dispersion of particles. The effects of various metal oxides on these properties will be discussed.

Introduction

The increased incorporation of thin polymer films into aerospace applications can be credited to their contribution to weight savings in spacecraft construction. The addition of particulate fillers to thin polymer films to make composites allows even more application as the properties of the composite can be potentially greatly improved over that of the neat polymer film. However, careful study is needed to ensure that in the effort to enhance certain properties in the composite, others that are also necessary to the application are not diminished.

The objective of this study was to determine what effects, if any, the distinct polymer/particulate systems and the method by which they were manufactured had on the elastic modulus of the thin film polymer composite. Additionally, optical microscopy was performed to discern qualitatively the degree of particulate dispersion within the polymer films.

Materials

Two different base polymers and three separate metal oxide powders were used in this study. The two base polymers were polyimides that have been classified as space durable. The first polyimide, TOR-NC, was prepared from stoichiometric amounts of oxydiphthalic dianhydride and 1,3-bis(3-aminophenoxy)benzene. The second polyimide, LaRCTM CP-2, was prepared from stoichiometric amounts of 4,4'-perfluoroisopropylidene dianhydride and 1,3-bis(3-aminophenoxy)benzene. The metal oxides, used in the preparation of these composites, were all commercially available nanoscale powders, namely antimony tin oxide (ATO, average particle size 11-29 nm, specific surface area 30-80 m²/g), indium tin oxide (ITO, average particle size 17-30 nm, specific surface area 40-70 m²/g), and yttrium oxide (Y₂O₃, average particle size 11-44 nm, specific surface area 19-80 m²/g).¹

These polymer composites were manufactured by two separate methods. The first method, denoted

(A), involved preparation of the polyimide first and then adding the metal oxide nanoparticles. The second method, denoted (B), consisted of the polymer and the metal oxide nanoparticles being prepared simultaneously.¹

Experimental Procedure

The specific combinations of base polymer and metal oxide filler and their respective glass transition temperatures (T_g) are presented in Table 1. The amount of metal oxide for each thin film polymer composite was approximately 3% by weight. Because the polymer/filler combination 3B, which consisted of 3% Y_2O_3 by weight in TOR-NC, experienced extreme embrittlement during manufacturing, no viable specimen was provided for mechanical characterization.¹

Dynamic mechanical analysis (DMA) was performed on all samples, using a Thermal Analysis 2980 dynamic mechanical analyzer with a tension film clamp installed. A photo of the test apparatus is shown in Figure 1. The film samples were cut to be between 5 and 6.5 mm in width and 20 and 30 mm in length to conform to the dimensional limits required for the tension film clamp. The average thickness for each film sample was based on three separate measurements at the two ends and the middle of the specimen with a Starrett Model 734 Electronic Digital Micrometer.

All samples were dried in a vacuum oven to remove any moisture and stored in a desiccator until testing. After mounting the sample in the DMA, the film sample was cooled to $-120\text{ }^{\circ}\text{C}$, using a flow of liquid nitrogen, and held for 5 minutes. The sample was then heated from $-120\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C}/\text{min}$. under a preload of 0.5 N. The samples were tested, using a dynamic force with a single frequency oscillation of 1 Hz and an amplitude of $20\text{ }\mu\text{m}$. At least three separate tests were run for each distinct film. The storage modulus for each run was calculated as a function of increasing temperature, using thermal analysis software included as part of the DMA.

Optical microscopy characterization was performed with a Nikon Eclipse ME600 transmission microscope outfitted with an X-Y translation stage to evaluate qualitatively the dispersion of particles within the polyimide films. A Nikon DXM 1200 digital camera was used to record the images. The sample was imaged in the as-received condition at a magnification of 200x.

Results and Discussion

Dynamic Mechanical Analysis

Figures 2 and 3 are composite graphs of temperature versus the storage modulus for each film, tested using DMA. Each film is represented by a single curve, considered typical of its test runs. In Figure 2, the TOR-NC polymer, a distinct separation in the storage modulus was shown between the A and B classes of films. The storage modulus of the clean (control) polymer film fell in between these two classes. In Figure 3, the LaRCTM CP-2 polymer, the storage modulus of all samples (with the exception of 5B) fell lower than that of the clean (control) polymer. For both materials, the storage modulus gradually diminished as the samples were slowly heated. The sudden drop in the storage modulus toward the end of the test was due to the onset of the glass transition in the polymer.

For every sample, the storage modulus for each individual test run at a given temperature was tabulated, and the average and standard deviation calculated. Table 2 shows the average storage modulus

and standard deviation for each film type at four specific temperatures in the test run. The scatter in the values is due to non-uniform thickness of the film samples and thermal instability of the DMA instrument at very low temperatures.

Optical Microscopy

Typical photomicrographs of both a TOR-NC and a LaRCTM CP-2 sample are shown in Figures 4 and 5, respectively. The images show agglomerates of the metal oxide additives randomly distributed throughout the polymer film. Since the changes in the storage modulus of the TOR-NC-based nanocomposites were dependent on the preparation method, the clumping of the individual metal oxide particles apparently had no influence. However, for the LaRCTM CP-2-based films, the clumping of the particles was a possible factor in the decrease in storage modulus for most of the samples.

Summary and Conclusions

Thin film polymer nanocomposites were characterized, using DMA and optical microscopy. More specifically, the films, manufactured by two distinct methods as combinations of two different polymers and three separate metal oxides, were evaluated to determine the storage modulus and degree of dispersion of nanoparticles, respectively. According to the analysis of the data, changes in the storage modulus for the TOR-NC-based nanocomposites were dependent on the method of manufacture as seen in the separation of the storage modulus curves by method group. Method A, where the particles were added to a prepared polyimide, produced samples with a higher storage modulus than the clean polymer. Method B, where the polymer and particles are prepared together, produced samples of decreased storage modulus compared to the clean polymer. However, in the case of the LaRCTM CP-2-based nanocomposites, storage modulus for most of the polymer/particulate systems was diminished by the addition of the metal oxide particles as the curves of all samples but one fell below that of the clean polyimide. The dispersion of the metal oxide particles within both polymers was shown by optical imaging to be poor with clumps of the particles non-uniformly distributed throughout each film. While this did not appear to adversely affect the storage modulus of the TOR-NC-based films, it seems to have been a contributor to the diminished storage modulus for the LaRCTM CP-2 samples.

References

1. Thompson, C. M., Herring, H. M., Gates, T. S., Connell, J. W., Preparation and Characterization of Metal Oxide/Polyimide Nanocomposites, Composite Science and Technology, Special Issue on Modeling and Characterization of Nanostructured Materials, ed. Thomas S. Gates, Elsevier, accepted for publication in 2002.

Table 1. Thermal Properties of Polymer-Metal Oxide Materials¹

Sample Number¹	Polymer	Additive (3% by wt.)	T_g², °C
	TOR-NC	None	212
1A	TOR-NC	ATO	210
1B	TOR-NC	ATO	203
2A	TOR-NC	ITO	202
2B	TOR-NC	ITO	197
3A	TOR-NC	Y ₂ O ₃	196
3B	TOR-NC	Y ₂ O ₃	209
	LaRCTM CP-2	None	203
4A	LaRC TM CP-2	ATO	192
4B	LaRC TM CP-2	ATO	194
5A	LaRC TM CP-2	ITO	195
5B	LaRC TM CP-2	ITO	200
6A	LaRC TM CP-2	Y ₂ O ₃	189
6B	LaRC TM CP-2	Y ₂ O ₃	206

1. A = Metal oxide powder added to polymer solution.
B = Polymer prepared in the presence of the metal oxide powder.
2. Determined on thin film by DSC at a heating rate of 10 °C/min.

Table 2. Average Storage Modulus (MPa)

	-100 °C		23 °C		100 °C		150 °C	
Sample	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.	Avg.	StDev.
Clean TOR-NC	4078.7	273.2	3200.0	308.4	2636.8	318.3	2255.7	269.5
1A	4101.0	250.4	3394.3	592.0	2901.7	488.1	2552.1	399.2
1B	3404.8	722.7	2626.2	865.1	2190.3	767.6	1919.6	667.5
2A	3399.8	332.6	2750.6	920.7	2392.1	724.7	2094.3	606.9
2B	2859.6	284.3	2167.0	183.7	1812.0	162.9	1588.3	147.0
3A	4297.4	540.8	3418.3	512.5	2846.7	458.0	2441.8	384.2
Clean LaRC™ CP-2	3178.7	539.0	3006.4	205.3	2565.9	189.6	2236.3	147.4
4A	2210.0	11.2	1809.8	50.2	1521.8	55.5	1350.5	44.0
4B	2716.1	241.2	2108.8	183.6	1699.8	56.3	1487.6	45.6
5A	2529.4	364.7	2117.1	107.9	1782.9	53.7	1592.3	53.3
5B	4150.0	612.7	3735.8	11.7	3185.1	8.0	2792.9	10.0
6A	2455.1	278.7	1932.2	135.1	1621.4	98.5	1438.9	85.2
6B	2898.6	734.6	1977.0	134.4	1746.9	128.7	1519.2	93.5

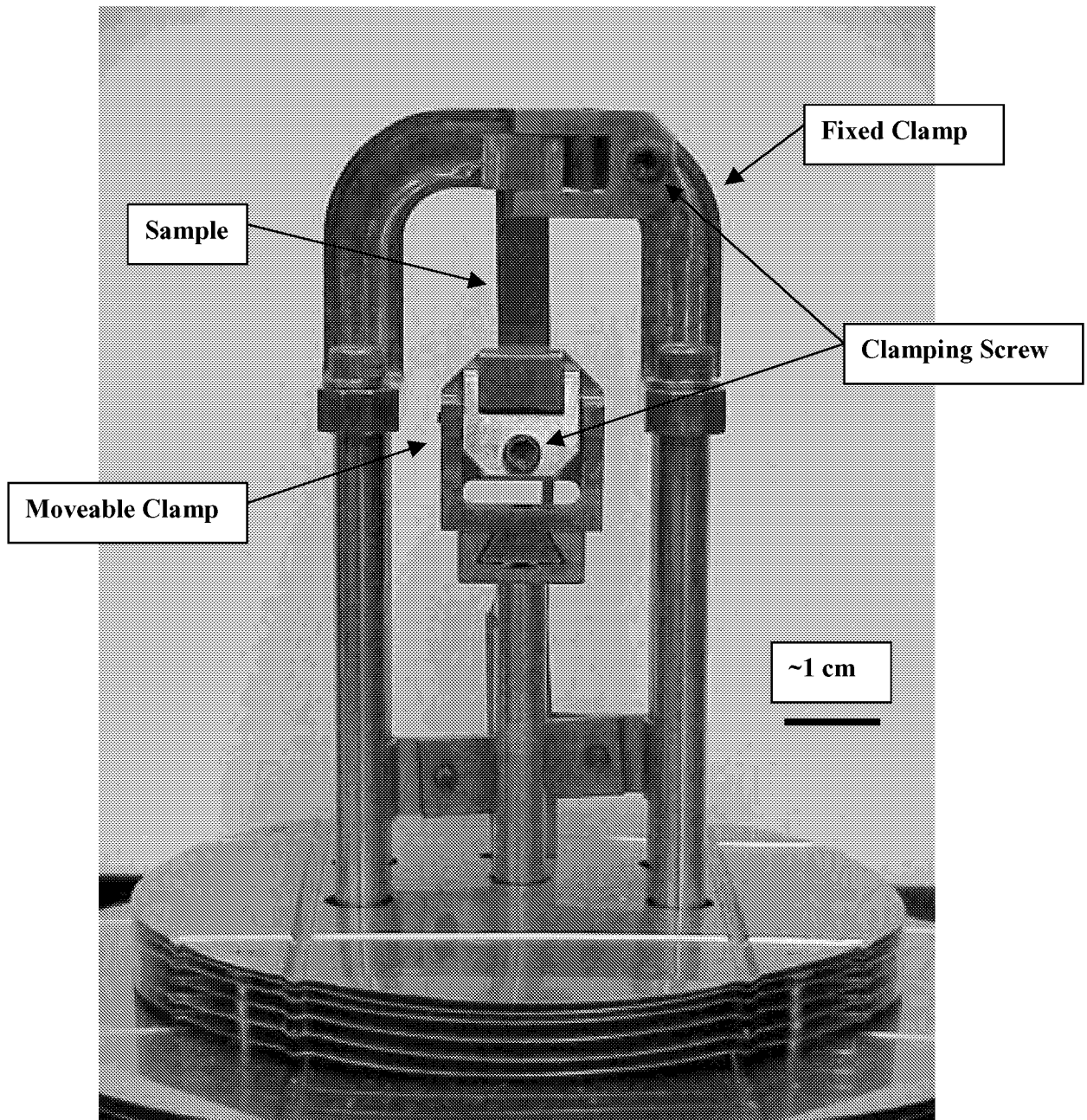


Figure 1. Dynamic Mechanical Analyzer with Tension Film Clamp Installed

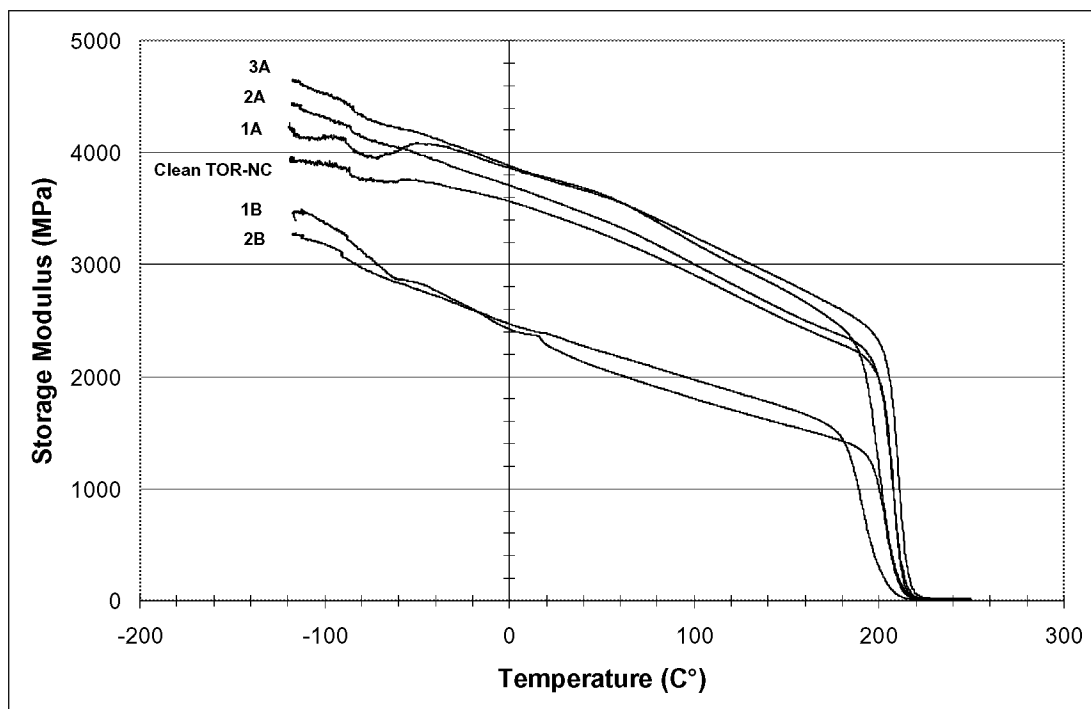


Figure 2. Temperature versus Storage Modulus for TOR-NC/Metal Oxide Nanocomposites

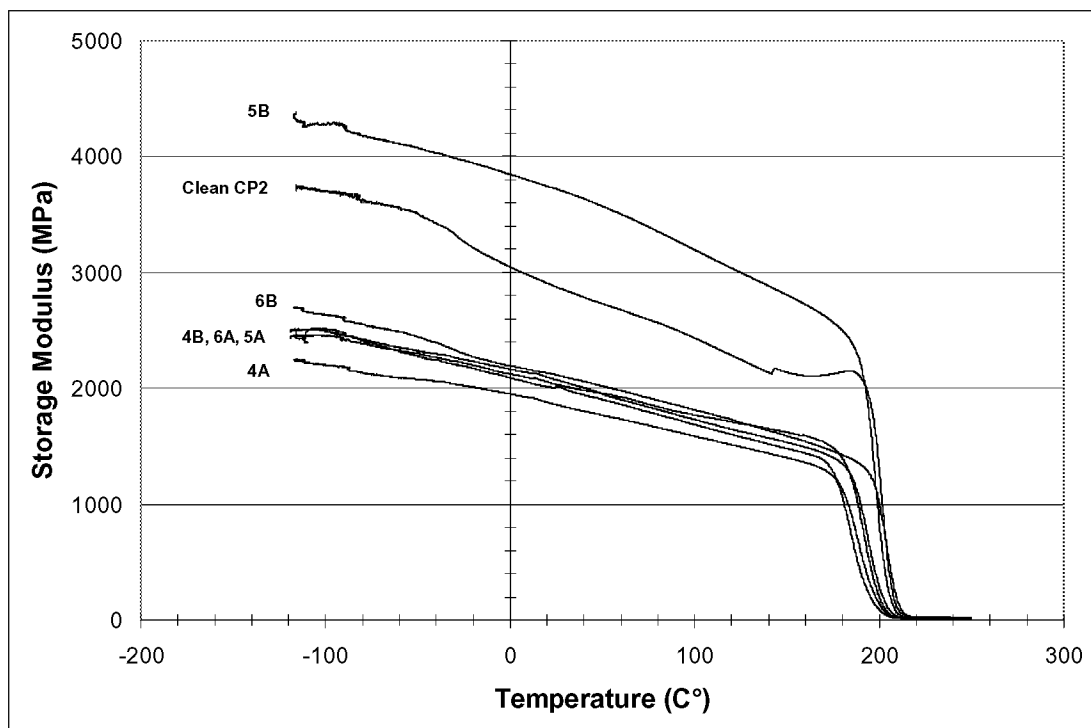


Figure 3. Temperature versus Storage Modulus for LaRC™ CP-2/Metal Oxide Nanocomposites

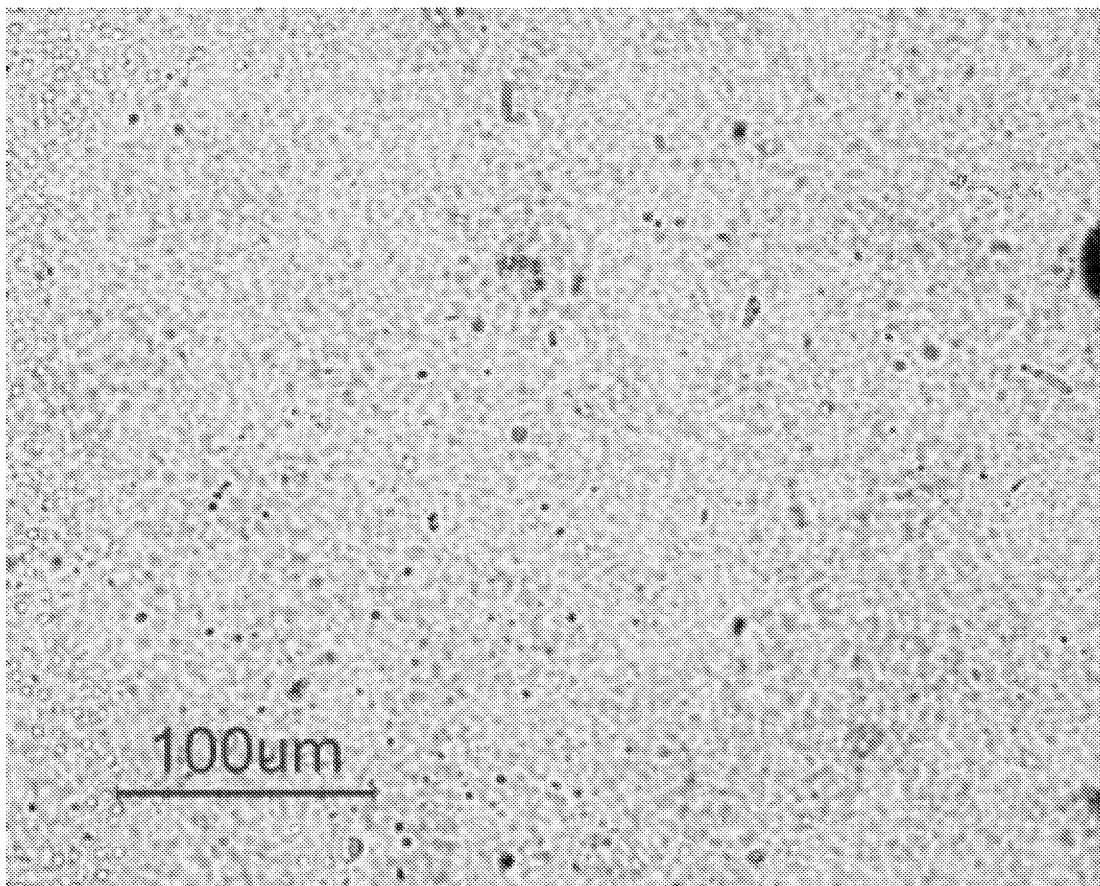


Figure 4. Optical Micrograph of Sample 1A (TOR-NC/ATO)

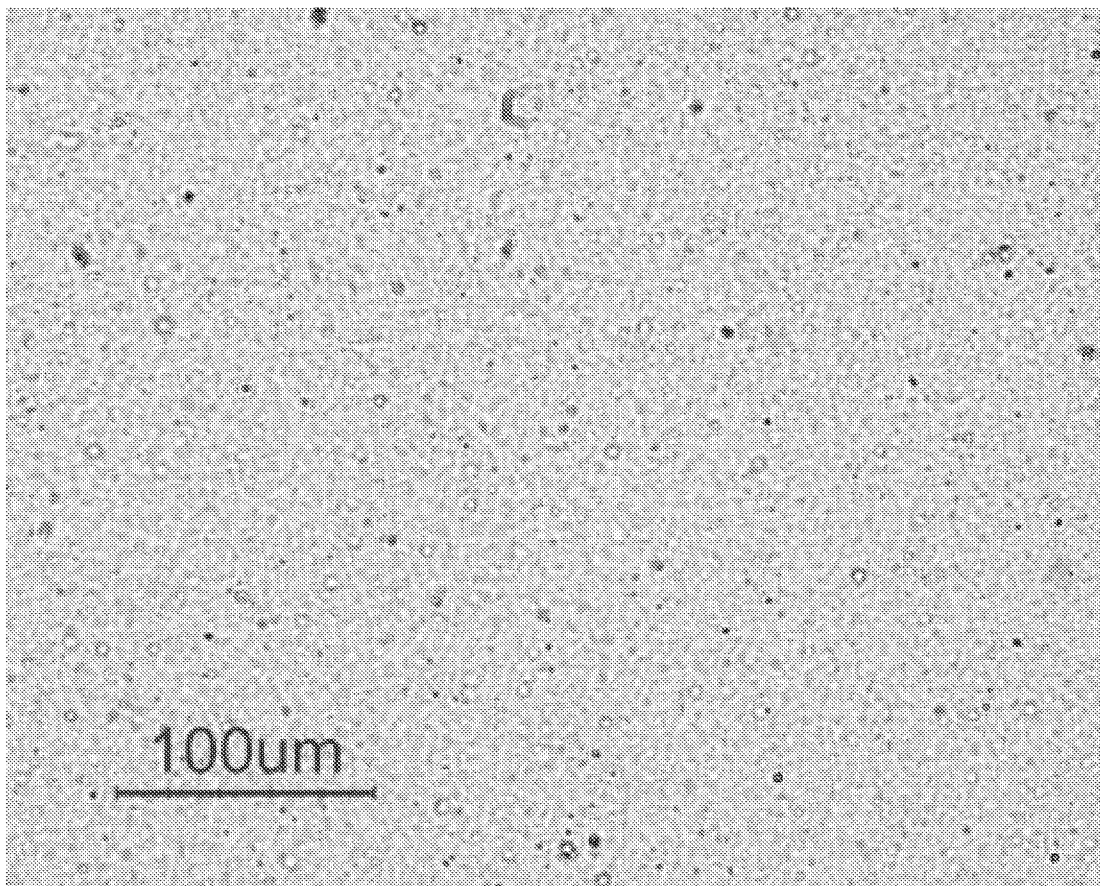


Figure 5. Optical Micrograph of Sample 5B (LaRC™ CP-2/ITO)

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 2003		3. REPORT TYPE AND DATES COVERED Contractor Report
4. TITLE AND SUBTITLE Dynamic Mechanical Characterization of Thin Film Polymer Nanocomposites			5. FUNDING NUMBERS NAS1-00135 762-30-51-03	
6. AUTHOR(S) Herring, Helen M.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Lockheed Martin Engineering & Sciences Hampton, VA 23681-2199			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Langley Research Center Hampton, VA 23681-2199			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA/CR-2003-212147	
11. SUPPLEMENTARY NOTES Langley Technical Monitor: Thomas S. Gates				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified-Unlimited Subject Category 24 Distribution: Nonstandard Availability: NASA CASI (301) 621-0390			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Many new materials are being produced for aerospace applications with the objective of maximizing certain ideal properties without sacrificing others. Polymer composites in various forms and configurations are being developed in an effort to provide lighter weight construction and better thermal and electrical properties and still maintain adequate strength and stability. To this end, thin film polymer nanocomposites, synthesized for the purpose of influencing electrical conductivity using metal oxide particles as filler without incurring losses in mechanical properties, were examined to determined elastic modulus and degree of dispersion of particles. The effects of various metal oxides on these properties will be discussed.				
14. SUBJECT TERMS Dynamic mechanical analysis; Optical microscopy; Thin film nanocomposites			15. NUMBER OF PAGES 15	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	